

THERMAL STABILITY OF POLYOXOMETALATE COMPOUND OF KEGGIN $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ SUPPORTED WITH SiO_2

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ABSTRACT

Synthesis through sol-gel method and characterization of polyoxometalate compound of $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ supported with SiO_2 have been done. The functional groups of polyoxometalate compound was characterized by FT-IR spectrophotometer for the functional groups and the degree's of crystallinity using XRD. The acidity of $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2$ was determined qualitative analysis using ammonia and pyridine adsorption and the quantitative analysis using potentiometric titration method. The results of FT-IR spectrum of $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ appeared at wavenumber 987.55 cm^{-1} (W=O), 864.11 cm^{-1} (W-Oe-W), 756.1 cm^{-1} (W-Oc-W), 3425.58 cm^{-1} (O-H), respectively and spectrum of $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\text{SiO}_2$ appeared at wavenumber 956.69 cm^{-1} (W=O), 864.11 cm^{-1} (W-Oe-W), 3448.72 cm^{-1} (O-H), respectively. The diffraction of XRD pattern of $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ and $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2$ compounds show high crystallinity. The acidic properties showed $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2$ more acidic compared to $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$. The qualitative analysis showed pyridine compound adsorbed more of polyoxometalate compound of $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2$. Analysis of stability showed that the $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2$ at temperature 500°C has structural changes compare to $200\text{-}400^\circ\text{C}$ which was indicated from vibration at wavenumber $800\text{-}1000\text{ cm}^{-1}$.

Keywords : $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$, polyoxometalate, SiO_2 .

INTRODUCTION

Polyoxometalate compound is the cluster compound of metal-oxygen which acid-base properties, it has various structural and oxidation rates, so it is very effective for both acid-base reaction and reduction oxidation reaction catalyst (Yamase dkk, 2002). Polyoxometallic compounds are effective as catalysts because they have higher acidity than sulfuric acid and not toxic (Okuhara *et al*, 1996). This compound has been applied as a catalyst in industrial processes in developed countries such as Japan (Nakagawa and Mizuno, 2007).

The research of polyoxometalate compounds are primarily intended in terms of its superiority as a catalyst which can be performed either in homogeneous or heterogeneous systems depending on the medium are used. In a heterogeneous system, the polyoxometalate compound can be used repeatedly in catalytic reaction.

The polyoxometalate compound has a low surface area and high solubility in a polar solvent (Kim *et al*, 2006). The Catalyst which have a small surface area is suitable for homogeneous catalysts while the homogeneous catalysts can not be recycled. To designed the polyoxometalate compound as a heterogeneous catalyst, modification should carried out by embedding. Modification of polyoxometalate compounds can be embedding by inclusion using both metal oxide and non-oxide metals (Nerwman *et al*, 2006). The embedding is carried out to have a large surface area which can be used as heterogeneous catalysis and can increase the acidity of the compound, so that the

catalytic properties increase. The catalytic activity is affected by the temperature, surface area, and acidity of the catalyst. The temperature affects collisions between molecules and certain chemical reactions require heating at high temperatures to obtain maximum results. As an example the hydroxylation reaction of n-hexane requires the temperatures above 400°C and requires the Bronsted acid side in the reaction to obtain a high percent conversion (Eid *et al*, 2013).

The synthesis of $\text{H}_4[\gamma\text{-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]$ has been carried out with various variations of embedding SiO_2 , TiO_2 , ZrOCl_2 and TaCl_5 by Karim (2014), which the product material has not been tested for its qualitative and quantitative acidity. Meanwhile Marci (et al 2013) has carried out the research by embedding Keggin $\text{H}_3\text{PW}_{12}\text{O}_{40}$ type polyoxometalate compounds with various metal oxides such TiO_2 , SiO_2 , ZrO_2 , ZnO , and AlO_2 . From the many several metal oxides which has been used, polyoxometalate compounds which are embedded with SiO_2 have higher catalytic character which applied to the propene hydration reaction.

In this research, the synthesis of Keggin $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ polyoxometalate compound which is embedded by SiO_2 metal oxide. The metal oxide of SiO_2 was obtained from reaction of tetraethyl orthosilical hydrolysis (TEOS) known as the sol gel method. The embedded result of synthesized polyoxometalate compounds were characterized by a *Fourier Transform Infra Red* (FT-IR) spectrophotometer and *X-Ray Diffractometer* (XRD). Polyoxometalate compounds $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ was soaked on the acid compounds before and after embedded qualitatively and quantitatively. The thermal stability character of $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ and $K_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2$ were tested by heating it at various temperature using furnace and the heating results were

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characterized by a FT-IR spectrophotometer. The acidity and thermal stability character of polyoxometalate compounds were tested prior to be used as catalysts in chemical reactions that require heating at high temperatures.

EXPERIMENTAL SECTION

The instruments which used in this research X-Ray diffractometer (XRD) Rigaku MiniFlex 600 and FT-IR Shimadzu Prestige-21 Spectrophotometer. The substances used in this research were sodium metasilicate ($\text{Na}_2\text{O}_3\text{Si}$), sodium tungstate (Na_2WO_4), hydrochloric acid (HCl), potassium chloride (KCl), potassium carbonate (K_2CO_3), tetraethyl orthosilika (TEOS), Sodium bis (2-Ethylhexyl) sulfosuccinate, cyclohexane, pyridine, ammonia (NH_3), n-butylamine, acetonitrile and aquades (H_2O).

Synthesis of Polyoxometalate Compounds $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and Its Characterization

The 11 g (50 mmol) $\text{Na}_2\text{O}_3\text{Si}$ compound was dissolved in aquades (100 mL) and 4M HCl depleted slowly to a pH range of 5-6 and stirred. The solvent was mixed with Na_2WO_4 of 182 g (0.55 mmol) which was dissolved with aquades (100 mL). The mixture was added with KCl of 80 g. With the addition of the mixture to be white and formed of sediment. After that, the mixture was filtered using filter paper, then the solid was dried to obtain the compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$. The solid obtained was white solid. The polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ was characterized by a FT-IR spectrophotometer and X-Ray diffractometer (XRD).

The synthesis $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ with Sol-gel Method and Its Characterization

The synthesis of compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ was modified from the procedure of (Kim *et al* 2006). Sodium bis (2-ethylhexyl) sulfosuccinate of 1.5 g was dissolved with 1 mL of cyclohexane (solvent A). The compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ of 0.76 g was dissolved with slightly aquades (solvent B). Solvent B is added to solvent A while distirer. A total of 11.2 mL of tetraethyl orthosilicate (TEOS) was added dropwise. Stirred with stirer and heated at 60 oC for 2 hours. The white solids formed are $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ and dried by vacuum. The compounds $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ are characterized by a FT-IR spectrophotometer, and X-Ray diffractometer (XRD).

The acidity test of compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ is qualitatively

A total of 0.5 g of each $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ were inserted into vials. A total of 10 mL of pyridine and 25% ammonia (NH_3) were each fed into a beaker glass. A vial bottle was inserted into a beaker glass containing pyridine and ammonia and then sealed tightly with a kreb plastic. The compound was allowed for two days to adsorption between pyridine and ammonia with polyoxometalate compounds. Compounds that have been in contact with pyridine and ammonia were tested qualitatively by characterizing using a FT-IR spectrophotometer.

The acidity test of compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$

A total of 0.1 g of each of the $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ were dissolved in 8 mL acetonitrile and stirred for 3 hours with a magnetic stirrer. The suspension was titrated with n-butylamine 0.05 M which was monitored by glass electrode as a pH sensor. Each droplet per volume of titrant was recorded to be the potential generated and connected between the volume of the titrant and the resulting potential. The classification of forces from the acidity side is classified on a scale of: $E > 100$ mV (very acidic); $0 > E > 100$ mV (acid side); $-100 < E < 0$ mV (weak acid side); And $E < -100$ mV (acid side is very weak).

The Thermal Stability Test $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$

The $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ was heated at 200 ° C, 300 ° C, 400 ° C and 500 ° C for 2 hours in the furnace. The heating compound was cooled and characterized by an FTIR spectrophotometer.

RESULTS AND DISCUSSION

Synthesis and Characterization of Keggin type

Polyoxometalate Compounds $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$

The synthesis of compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ was performed by addition of potassium chloride (KCl) to the compound $[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ acting as a K^+ ion donator. At the end of the synthesis process there was obtained a white solid which was a compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$. The result of synthesis in the form of white solid was then characterized using FT-IR spectrophotometer which aims to identify the functional group formed as shown in Figure 1.

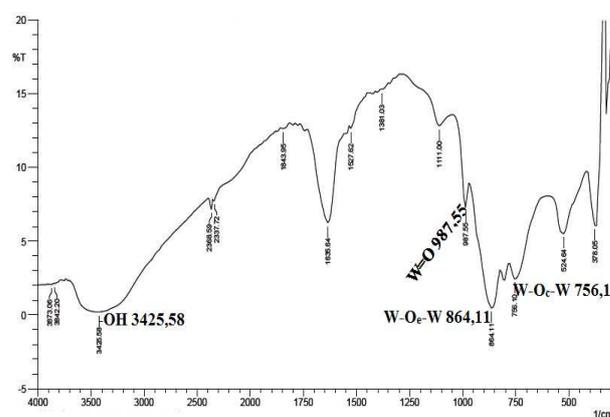


Figure 1. FTIR spectra of polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$

The peaks of the functional groups of polyoxometalate compounds appearing at wave numbers 4000-300 cm^{-1} shows in Figure 1. The principal uptake of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ compounds shows the presence of vibration $\text{W} = \text{O}$ appears in the 987.55 cm^{-1} region, the W-O-W vibration of 864.11 cm^{-1} in which oxygen is located on the edge of the compound Polyoxometalate and wave number 756.1 cm^{-1} for the vibration of the W-O-W group which is the oxygen atom located at the center of the polyoxometalate compound. According to Okuhara (*et al* 2001), the absorption of polyoxometalate compounds has $\text{W}=\text{O}$ groups at wave number 980 cm^{-1} ,

vibration of W-O_c-W group 878 cm⁻¹, and vibration of W-O_c-W 779 cm⁻¹. The compound K₈[β₂-SiW₁₁O₃₉]·nH₂O synthesis results in this study is in accordance with vibrations according to Okuhara (*et al* 2001). In addition to the 3425.58 cm⁻¹ wave numbers indicating the vibration -OH which indicates the presence of H₂O in the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O. The presence of a hydrogen bonding effect is characterized by a widened peak in the FT-IR spectrum of Stuart (2004). K₈[β₂-SiW₁₁O₃₉]·nH₂O.

After the compound K₈[β₂-SiW₁₁O₃₉]·nH₂O was characterized using FT-IR spectrophotometer, then the polyoxometallic compound K₈[β₂-SiW₁₁O₃₉]·nH₂O was analyzed by XRD. Diffractogram of K₈[β₂-SiW₁₁O₃₉]·nH₂O polyoxometalate compound · nH₂O is presented in Figure 2.

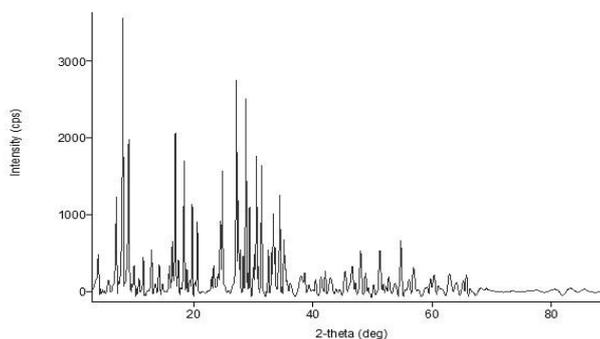


Figure 2. XRD Diffractogram Patterns Polyoxometalate Compound K₈[β₂-SiW₁₁O₃₉]·nH₂O

Figure 2 shows the diffraction for the polyoxometalate compounds K₈[β₂-SiW₁₁O₃₉]·nH₂O with the highest intensity arising at 8°, 9°, 17°, 24° and 35° diffraction angles. According to Yang (*et al* 2011) the diffraction for polyoxometallic compounds is present in some diffraction regions, ie 6-10°, 15-20°, 22-25°, and 35-40°. The diffraction that appears below 10° in region 2θ shows that the polyoxometalate compound has a very high crystallinity. Diffractogram of K₈[β₂-SiW₁₁O₃₉]·nH₂O compounds exhibiting sharp diffraction peaks indicates polyoxometalate K₈[β₂-SiW₁₁O₃₉]·nH₂O has very high crystalline properties in which the atoms of the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O is arranged regularly based on the length and angle of regular bonding.

Synthesis of Keggin Type Polyoxometalate Compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ and Characterization

The polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O which has been obtained was further prepared by proportion to SiO₂ obtained from TEOS hydrolysis. The embodiment was carried out by using a microemulsion and sol-gel method. Eriksson (*et al* 2004) describes that microemulsions are liquids derived from a mixture of water, hydrocarbons, and surfactants. Polyoxometalate compounds K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ synthesis and characterization by functional group analysis using FT-IR spectrophotometer with FT-IR spectra presented in Figure 3. The result of identification using FTIR spectrophotometer to compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ shows the specific vibration of polyoxometallic and SiO₂ compounds.

Figure 3 shows the difference shown by the FT-IR spectrum of the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O before being carried out with SiO₂. According to Derrick (*et al* 1999) the symmetric vibration of Si-O-Si is at the wave number 1130-1000 cm⁻¹. Smith (1999) reported that the vibration of Si-O-Si symmetric stretching was stronger at 1085 cm⁻¹. The FTIR spectra of compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ undergo a shift of wave numbers for asymmetric Si-O-Si stretch vibration at 1103.28 cm⁻¹. The shift of wave numbers occurs in vibration W=O. The W=O vibrate before it is presented appears at the wave number 987.55 cm⁻¹ and the vibration after carrying with SiO₂ appears at the wave number 956,69 cm⁻¹. According to Stuart (2004) vibration -OH vibration in the presence of hydrogen bonding effect is in the range of 3500-2500 cm⁻¹ wavelength characterized by a widened peak on the FT-IR spectra. Figure 3 (B) experiences a shift in the number of waves at the peak of 3448.72 cm⁻¹ identifies the -OH vibration by the presence of H₂O on the K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ and the wave number at peak 3425.58 cm⁻¹ identifies vibration -OH by the presence of H₂O in the compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. The primary wave numbers of K₈[β₂-SiW₁₁O₃₉]·nH₂O and K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ are presented in Table 1.

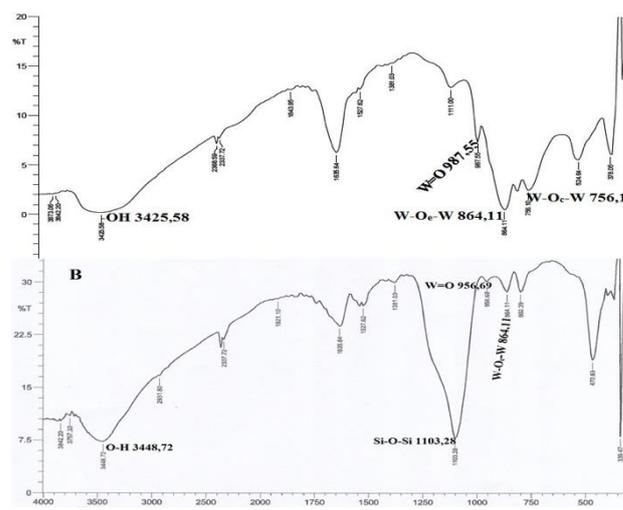


Figure 3. FTIR spectra of polyoxometallic compound K₈[β₂-SiW₁₁O₃₉]·nH₂O (A), FT-IR spectra of polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ (B)

Table 1. Wave number K₈[β₂-SiW₁₁O₃₉]·nH₂O and K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂

| Vibration K ₈ [β ₂ -SiW ₁₁ O ₃₉]·nH ₂ O (cm ⁻¹) | Vibration K ₈ [β ₂ -SiW ₁₁ O ₃₉]·nH ₂ O/SiO ₂ (cm ⁻¹) | Type of Vibration |
|---|--|---------------------|
| 987.55 | 956.69 | W=O |
| 864.11 | 864.11 | W-O _c -W |
| 756.1 | - | W-O _c -W |
| 3425.58 | 3448.72 | O-H |
| - | 1103.28 | Si-O-Si |

The polyoxometalate compound · K₈[β₂-SiW₁₁O₃₉]·nH₂O which was supported with SiO₂ then characterized using XRD. The diffraction angle and crystallinity of polyoxometalate compounds K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. Comparison of XRD of compound K₈[β₂-SiW₁₁O₃₉]·nH₂O with K₈[β₂-

$\text{SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ are presented in Figure 4. (A) $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ diffraction emerging below 10° in region 2θ indicates that the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ has very high crystalline properties due to the atom of the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ is arranged regularly based on the length and angle of bond formed. Figure 4 (B) shows the XRD pattern of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$. The compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ has a high crystallinity with a diffraction angle of 2θ each at 8° , 18° , 27° , and 34° indicating the characteristics of the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ in which the atoms of the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ were arranged regularly on the basis and length of the regular bonding. Figure 4 (B) shows the pattern of XRD $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ indicating a change in the diffraction angle.

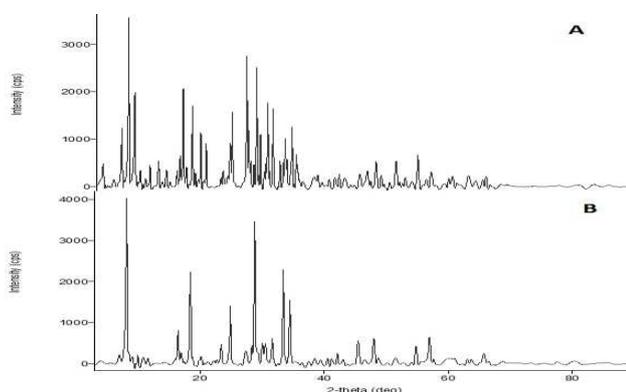


Figure 4. The diffraction pattern of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ (A), diffraction pattern of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ (B)

The acidity test of compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ and $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ in qualitatively

The Acidity test of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$

The acidity measurement of the polyoxometalate compound $\cdot \text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ is carried out both qualitatively and quantitatively. The FT-IR spectrophotometer method was performed for qualitatively, where $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ polyoxometalate compound was saturated with ammonia and with pyridine for 2 days resulting in adsorption on the surface of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$. The saturation result were compared before or after being saturated with ammonia or pyridine. The saturation result was measured by a FTIR spectrophotometer. The FTIR spectra $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ saturation result shown in Figure 5.

Polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ of the FT-IR spectra of Figure 5 shows no absorption bands at $1400\text{-}1440\text{ cm}^{-1}$ wavelengths on a $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ saturated polyoxometalate compound with or without saturation Pyridine. According to Dines (*et al*, 1991) ammonia forms ammonium ions (NH_4^+) with the observed wave numbers at $1400\text{-}1440\text{ cm}^{-1}$, but in the polyoxometalate compound $\cdot \text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ not exhibit ammonium ion vibrations (NH_4^+) at wave number $1400\text{-}1440\text{ cm}^{-1}$. Ammonia can be adsorbed on the acid side of the heteropoly compound and in the metal

cation (Seo *et al*, 1988). Ammonia was not adsorbed on the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$. It was possible that the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ does not exhibit ammonium ion vibration (NH_4^+) at wave numbers $1400\text{-}1440\text{ cm}^{-1}$. Figure 5 (B) shows a vibration of $-\text{OH}$ at a wave number of 3448.72 cm^{-1} which identifies the presence of H_2O in a polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$. According to Stuart (2004), vibration $-\text{OH}$ vibration, with the effect of hydrogen bonds in the range of $3500\text{-}2500\text{ cm}^{-1}$ wavelengths characterized by wider peaks in the FT-IR spectra.

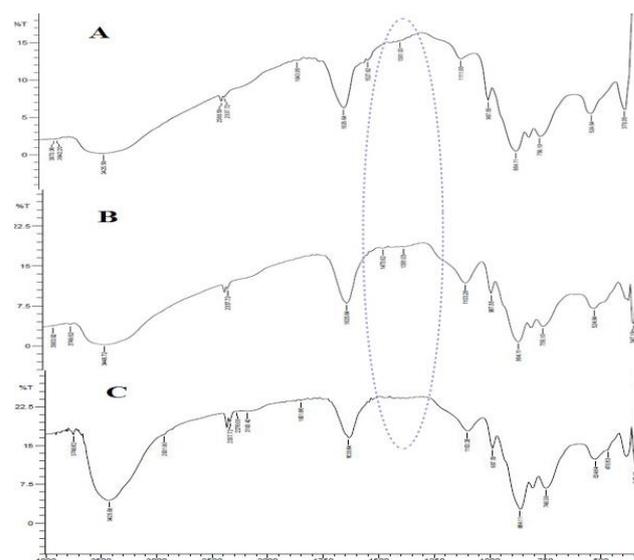


Figure 5. FTIR spectrum of polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ (A), FTIR spectra of polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$. Saturation with ammonia (B), FT-IR spectra of polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ saturation with pyridine (C)

Polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ compounds with saturation with pyridine in Figure 5 (C) exhibit an $-\text{OH}$ shift vibration appearing at a 3425.58 cm^{-1} wave number identifying H_2O in a polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$. According to Khalifah and Prasetyo (2008) pyridine molecules bound to Lewis acid sites absorbed at wave numbers $1400\text{-}1700\text{ cm}^{-1}$. Figure 5 (C) FT-IR spectra does not show the wave number. In this case, pyridine was unadsorbed in the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$. FT-IR digital specimen data of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ compounds with saturation with ammonia and pyridine.

The Acidity Test of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$

The compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ was saturated using ammonia and pyridine. Then the material was characterized by an FT-IR spectrophotometer. The saturation result was measured by an FTIR. The FT-IR spectra of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ of the saturation results are shown in Figure 6.

Figure 6 (A) shows the FTIR spectra of a polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ before being saturated. Figure 6 (B) shows the FTIR spectra of a polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}/\text{SiO}_2$ with saturation using

ammonia. Dennis (*et al* 1991) states that ammonia forms an ammonium ion (NH_4^+) with an observed wave number at $1400\text{--}1440\text{ cm}^{-1}$. Seo (*et al* 1988) states that ammonia can be adsorbed on the acid side of the heteropoly compound and in the metal cation. The compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ exhibits the vibration of the NH_4^+ ammonium ion appearing at the wave number 1404.18 cm^{-1} .

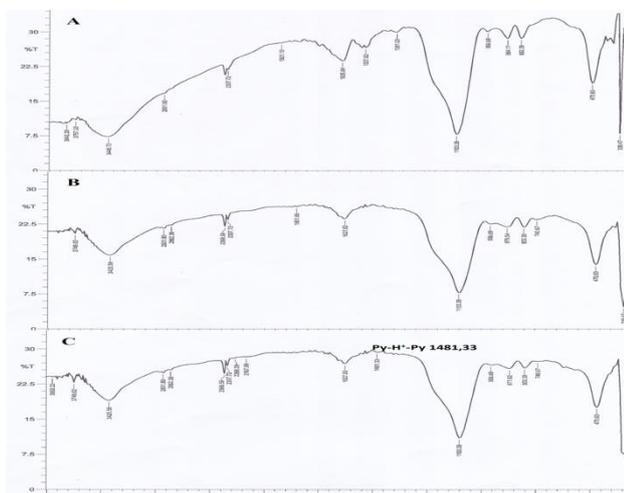


Figure 6. FTIR spectra of polyoxometalate compounds $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ (A), FT-IR spectra of polyoxometalate compounds $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$. Saturation with ammonia (B), FT-IR spectra of polyhydroxide compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ saturation with pyridine (C)

Polyoxometalate compounds $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ saturated with ammonia absorbance bands not found at wavelength $1400\text{--}1440\text{ cm}^{-1}$. In this case it is possible that the ammonia was not adsorbed on the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$. Stuart (2004) states that vibration -OH vibration in the presence of hydrogen bonding effect is in the range of $3500\text{--}2500\text{ cm}^{-1}$ wavelengths characterized by a widened peak on the FTIR spectra. Polyoxometalate compounds $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ exhibit a -OH loop vibration at 3425.58 cm^{-1} wave numbers identifying the presence of H_2O in the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$.

Figure 6 (C) shows the spectra of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ compounds with saturation using ammonia also exhibiting a -OH looping vibration at a 3425.58 cm^{-1} wave number that identifies the presence of H_2O in the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$. The Caliph and Prasetyoko (2008) explain that pyridine molecules bound to Lewis acid sites are adsorbed at wave numbers $1400\text{--}1700\text{ cm}^{-1}$. Picture no. 10 (C) shows that the pyridine molecule has been adsorbed by the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ shown in the wave number 1481.33 cm^{-1} . This shows that the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ has Lewis acid character.

Based on the FTIR spectrum of Figure 5 and 6, it can be seen that the wave number 1404.18 cm^{-1} is a vibration of the ammonium ion NH_4^+ . The compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ saturated with ammonia (Figure 6 B) does not show the uptake of ammonia molecules at the 1404.18

cm^{-1} wave number as well as the compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ (Figure 5 B). In this case the ammonia is not adsorbed on the compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and the compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$. The FT-IR spectra at Figure 5 (C) does not show the uptake of pyridine molecules at the 1404.18 cm^{-1} wave number while the FT-IR spectra of Figure 6 (C) of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ see the wave number $1481,33\text{ cm}^{-1}$ but does not show sharp spectra. It can be concluded that qualitatively pyridine adsorbed more on the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$.

The acidity test of compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ in Quantitative

The acidity measurements of the $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ compounds were quantitatively measured by titration of potentiometric potassium using *n*-butylamine as titrant and acetonitrile as solvent. Acetonitrile is an aprotic solvent as a solvent on the compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ so that only the acidity of $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ and $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$. According to Pecchi (*et al* 1985) using benzene solvent, acetonitrile and iso-octane as solvents in potentiometric titration and selected acetonitrile as a polar solvent to avoid the adsorption of *n*-butylamine and acetonitrile as an inert solvent

The measurement by potentiometric method can determine the total acidity and acidity strengths of a polyoxometalate compound. The initial potential value (E_i) identifies acidity strength from the surface side and classifies the acidity strength based on the range that classifies in scale: $E_i > 100\text{ mV}$ (acidity is very strong), $0 < E_i < 100\text{ mV}$ (strong acidity), $-100 < E_i < 0\text{ mV}$ (weak acidity), $E_i < -100\text{ mV}$ (acidity is very weak) (Romanelli *et al*, 2004). The first derivative curve and the second derivative are made to be able to see where the titration equivalent point is shown in Figure. 11 The equivalent point was performed to see the condition in which the base of *n*-butylamine is added precisely reacts with the acidic $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ which was titrated. In addition, an equivalence point is performed to determine the amount of base volume of *n*-butylamine required to neutralize $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ acid.

Figure 7 shows the results of measurement of the compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ has an initial potential value of 54.4 mV . Based on the potential value range of $0 < E_i < 100$ the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$ has a strong acid side. The titration equivalent point is at 0.2 mL of *n*-butylamine volume reinforced by the first derivative curve and the second derivative of potentiometric titration. The titration equivalent point can be observed with sharp potential changes (Mulja and Suharman, 1995). Figure 8 and 9 show the first derivative curves and the second derivative curves of the polyoxometalate $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}$.

The measurement of the acidity level of the polyoxometalate compound $\text{K}_8[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot\text{nH}_2\text{O}/\text{SiO}_2$ is also carried out through potentiometric titration. From the titration curve presented in Figure 10, the titration equivalent point was obtained at the time of titration volume of 0.4 mL *n*-butylamine. Based on the data of the equivalence point it is found that the

polyoxometalate $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ compound requires more base volume of n-butylamine to neutralize the polyoxometalate compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$. This indicates that $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ is more acidic than a polyoxometalate compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$. This is also supported by looking at the potential initial value comparison. The initial potential value of $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ ions is 76.6 mV whereas the initial potential value of $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ compounds is 54.4 mV. The compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ is included in the acidic acid classification strong based on the potential value range of acid strength. Increased density of polyoxometalate compounds $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ because the compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ interacts with the carrier SiO_2 .

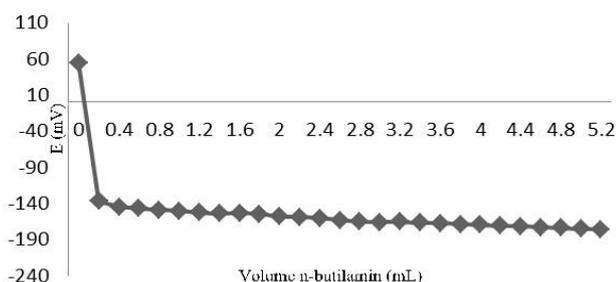


Figure 7. Potentiometric titration curve of compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$

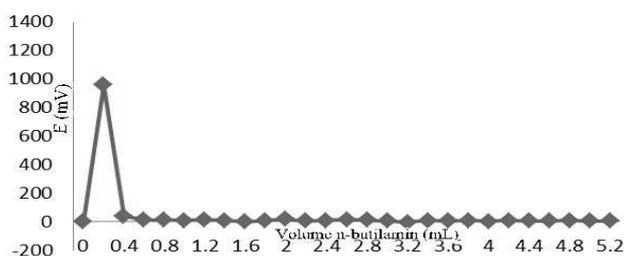


Figure 8. The first titular titration curve of potentiometric titration of compound $K_8[\beta_2SiW_{11}O_{39}] \cdot nH_2O$

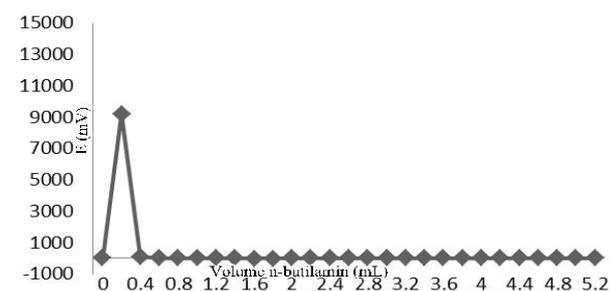


Figure 9. The second titular titration curve of potentiometric titration of compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$

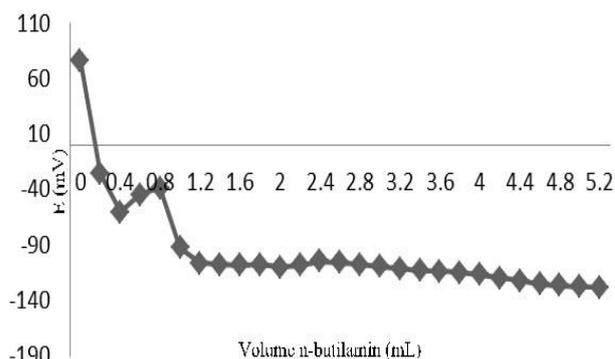


Figure 10. Potentiometric potentiometric curve of compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$

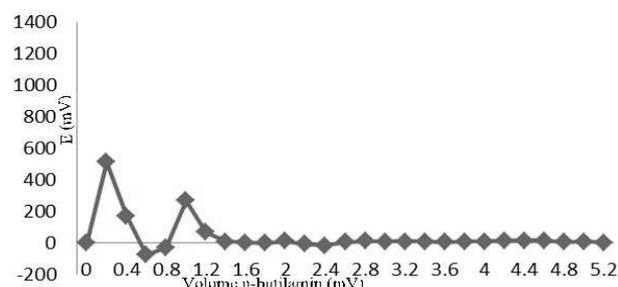


Figure 11. The first derivative titration curve, potentiometric titration of compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$

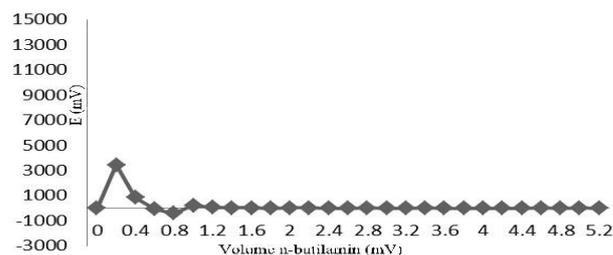


Figure 12. The second derivative titration curve, potentiometric titration of compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$

Potentiometric titration method is an analytical technique based on the potential measurement of a sensor or electrode. The electrodes used are glass-containing glassed electrode, the liquid having the potential difference properties between the membrane and the electrolyte in contact with the membrane is determined by the activity of the particular ion. The membrane electrode used is a glass electrode. These glass electrodes are said to be ion-selective because they are specific only to H^+ ions. Potential measurements of polyoxometalate compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ can be performed with potentiometric titration because the compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ has H^+ ions. Potentiometric titration curve of $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ can be seen in Figure 10.

The thermal Stability Compound of $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$

The compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ of results the preparation was heated at various temperatures to see the thermal stability of $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$. The heating results at various temperatures were characterized by FTIR

spectrophotometers. Figure 13 shows the FT-IR spectra of the wavelengths that appear on the $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ and $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ unheated and heated at various temperatures from 200-500°C.

Figure 13 shows the difference shown by the FT-IR spectra of the $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ compound before being carried out with SiO_2 or after heating. Based on the FTIR spectrum the warming of vibrations emerging undergoes a shift in the number of waves. Figure 13 (A) and (B) show the wave numbers 3425.58 cm^{-1} and 3448,72 cm^{-1} while in Figure 13 (C), (D), (E) and (F) indicate wave numbers 3433,29 cm^{-1} , 3441,01 cm^{-1} , 3425,58 cm^{-1} , 3402,43 cm^{-1} are identified as -OH groups in the presence of H_2O with a slight amount seen from percent transmittance. Figure 13 (F) shows excellent thermal stability properties in the presence of small amount of H_2O which was characterized by a shift in the wavelength number of the -OH group. The vibration of polyoxometalate compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ in the 800-1000 cm^{-1} wave range at 500°C shows slight differences due to vibration $W=O$ overlapping with vibrations $W-O_e-W$ and $W-O_c-W$. This suggests that on increasing the heating temperature may cause changes in the structure of polyoxometalate compounds. Table 2 shows the vibrations of the $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$, $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ without heating and after heating at a temperature of 200°C - 500°C.

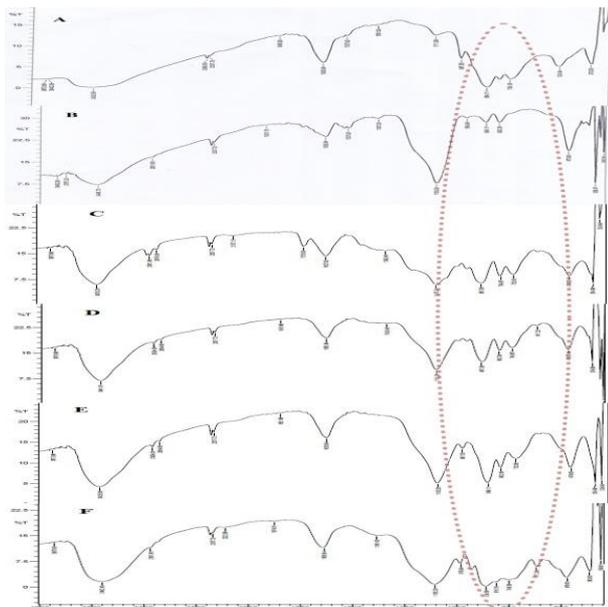


Figure 13. FT-IR spectra of polyoxometallic compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ (A), FT-IR spectra of polyoxometalate compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ (B), FT-IR spectra of polyoxometalate compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ of heating at 200°C (C), 300°C (D), 400°C (E), 500°C (F).

Table 2. Wave number of compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$, $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ without heating and heating at a temperature of 200°C-500°C

| $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ | $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ | Vibration |
|---|---|-----------|
| 3425.58 | 3448.72 | -OH |
| 3433.29 | 3441.01 | -OH |
| 3425.58 | 3425.58 | -OH |
| 3402.43 | 3402.43 | -OH |

| | 200° | 300° | 400° | 500° | | |
|--------|---------|------|------|------|------|-------------------|
| | C | C | C | C | | |
| 987.55 | 956.69 | - | - | 987. | 979. | W |
| 864.11 | 864.11 | 887. | 887. | 5 | 8 | W=O |
| 756.1 | - | 2 | 2 | 864. | 858. | W W- |
| 3425.5 | 3448.72 | 794. | 740. | 1 | 3 | O _c -W |
| 8 | | 6 | 6 | 732. | 748. | WW- |
| | | 3433 | 3441 | 9 | 3 | O _c -W |
| | | .2 | .0 | 3425 | 3402 | Si- O- |
| | | | | .5 | .4 | H |

CONCLUSION

Polyoxometalate compounds $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ and $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ were synthesized. The main vibration of the IR spectra of $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ shows the presence of vibration $W=O$ appears in the area of 987.55 cm^{-1} . $W-O_e-W$ appears in the area of 864.11 cm^{-1} , $W-O_c-W$ appears in the area of 756.1 cm^{-1} , O-H, OH appears in the area of 3425.58 cm^{-1} and for the compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ vibration $W=O$ appears in the region 956.69 cm^{-1} , $W-O_e-W$ appears At 864.11 cm^{-1} and -OH area appears at 3448.72 cm^{-1} . The XRD diffraction pattern for $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ differs at the diffraction angles of 8°, 9°, 17°, 24°, 35° and for the compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ appears at the angle of diffraction of 2θ each of 8°, 18°, 27°, and 34°. Polyoxometalate compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ with a potential value of 76,6 mV has a higher acidity value than the compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ having a potential value of 54.3 mV. Qualitative analysis by using ammonia and pyridine to compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O$ and $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ it was found that the pyridine compound adsorbed more on the polyoxometalate compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$. The thermal stability test of the compound $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ shows at a temperature of 500°C of $K_8[\beta_2-SiW_{11}O_{39}] \cdot nH_2O/SiO_2$ compound slightly altered the structure of the polyoxometalate compound characterized by overlapping of vibrations in the range of 800-1000 cm^{-1} .

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